

PHOTOLUMINESCENCE EXCITATION SPECTROSCOPY OF CARBON-DOPED GALLIUM NITRIDE

E. E. Reuter*, R. Zhang**, T. F. Kuech**, S. G. Bishop*

*University of Illinois Microelectronics Lab, 208 N. Wright St., Urbana, IL 61801

**Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706

Cite this article as: MRS Internet J. Nitride Semicond. Res. 4S1, G3.67 (1999)

ABSTRACT

We have done a comparative study of carbon-doped GaN and undoped GaN utilizing photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopies in order to investigate deep levels involved in yellow luminescence (YL) and red luminescence (RL). When the GaN was excited by above-bandgap light, red luminescence (RL) centered at 1.82 eV was the dominant below-gap PL from undoped GaN, but carbon-doped GaN below-gap PL was dominated by yellow luminescence (YL) centered at 2.2 eV. When exciting PL below the band-gap with 2.4 eV light, undoped GaN had a RL peak centered at 1.5 eV and carbon-doped GaN had a RL peak centered at 1.65 eV. PLE spectra of carbon-doped GaN, detecting at 1.56 eV, exhibited a strong, broad excitation band extending from about 2.1 to 2.8 eV with an unusual shape that may be due to two or more overlapping excitation bands. This RL PLE band was not observed in undoped GaN. We also demonstrate that PL spectra excited by below gap light in GaN films on sapphire substrates are readily contaminated by 1.6-1.8 eV and 2.1-2.5 eV chromium-related emission from the substrate. A complete characterization of the Cr emission and excitation bands for sapphire substrates enables the determination of the excitation and detection wavelengths required to obtain GaN PL and PLE spectra that are free of contributions from substrate emission.

INTRODUCTION

The most common deep, below-gap luminescence that has been observed in GaN is the yellow luminescence (YL), a broad band centered at about 2.2 eV which appears in most published photoluminescence (PL) spectra of GaN [1-5]. The cause of the YL has been attributed to intrinsic crystal defects [3] and to impurities such as carbon [1,2], to a Ga-site vacancy and related complexes [6,7], or to a combination of several mechanisms [5]. It has also been found that the YL is far less intense in GaN grown by hydride vapor phase epitaxy (HVPE) than in GaN grown by metal organic chemical vapor deposition (MOCVD), and it should be noted that HVPE growth of GaN does not involve carbon containing source materials [8]. Another deep, below-gap PL band has been observed in GaN grown by HVPE and is centered at about 1.8 eV [9,10]. This weak red luminescence (RL) band is difficult to observe in GaN that has strong YL which may explain why RL is usually reported only from GaN grown by HVPE.

Two mechanisms have commonly been suggested to explain the YL in GaN. The mechanism with the widest acceptance involves a radiative transition from a shallow donor level to a deep acceptor level with a depth of 860 meV or to a deep double donor or V_{Ga} and related complexes. [2,3,6,7]. A second proposed mechanism is a transition from a deep double donor to a shallow acceptor [4]. Recent experiments have suggested that there may be more than one recombination channel responsible for the YL [5], with the specific channels present depending on the measurement temperature and how the GaN was grown. While many shallow and deep defect- and impurity-related levels have been reported for GaN [2, 10, 12, 13, 14, 16],

specific associations of these levels with proposed models for the YL have not been definitively proven.

It is important to note that the sapphire substrates often used for growing GaN usually contain Cr^{3+} impurities which contribute to a broad PL emission from the substrate in the same spectral region as the YL from GaN. Sapphire containing Cr^{3+} also exhibits a sharp line emission at 1.79 eV when pumped in the broad Cr^{3+} absorption bands centered at 2.2 eV and 3.0 eV [15]. When luminescence is excited by photons with energy below the bandgap of GaN from samples consisting of thin (several micron thick) GaN epilayers grown on thick sapphire substrates containing Cr^{3+} , the luminescence observed can be a mixture of emission from the substrate and the GaN and in some cases may be primarily from the substrate.

Ideally PL and photoluminescence excitation (PLE) spectroscopy excited with photon energies below the GaN bandgap would be performed on free-standing GaN epilayers removed from their substrates. However, the substrate removal is difficult and PL and PLE measurements are routinely performed on thin films still mounted on their substrates [3,17]. Some workers have pointed out that even when PL is pumped with photon energies above the GaN bandgap, it is possible for intense GaN PL in the blue spectral range to excite Cr^{3+} luminescence from the sapphire substrate [15]. Although the excitation of substrate emission is even more probable for direct optical pumping below the GaN bandgap, several PLE investigations of GaN in the below-gap spectral range have been reported in which 3-5 micron thick epitaxial layers of GaN on sapphire substrates were employed [3,17]. These publications make no mention of precautions to avoid distortion of the PLE spectra by substrate emission which complicates the interpretation of their reported PLE lineshapes and low energy thresholds.

The present work demonstrates the effectiveness of PLE spectroscopy in the investigation of optical absorption and emission below the bandgap of GaN. PLE spectroscopy involves detecting luminescence intensity at a selected wavelength within a luminescence band as a function of the wavelength of the exciting light, thus isolating one luminescence band and providing information about the absorption energies required to excite that luminescence band. Above-gap excitation of GaN typically produces broad, featureless, mid-gap PL spectra comprising multiple, overlapping YL and RL bands from deep defect or impurity levels [2, 9, 11]. PLE spectroscopy in the below-gap spectral range can detect extrinsic absorption bands which selectively and separately excite these overlapping PL bands. In the work presented here, the selective excitation isolates a broad RL band associated with C-doping, enabling its PL and PLE spectra to be obtained without interference from overlapping emission bands. In addition, we characterize the PL and PLE of the sapphire substrate in order to obtain a complete understanding of the potential influence of sapphire substrate emission on GaN PL and PLE.

EXPERIMENT

GaN samples were grown on (0001) sapphire substrates using NH_3 , Ga, and HCl, and some samples were doped with carbon by introducing C_2H_2 into the reactor, as described in detail elsewhere [5]. These samples were 30 μm to 50 μm thick. Hall measurements showed that both the undoped and the C-doped samples were n-type with a concentration of $4 \times 10^{18} \text{ cm}^{-3}$. The undoped samples were analyzed by secondary ion mass spectroscopy (SIMS) and found to have a carbon concentration of less than $2 \times 10^{16} \text{ cm}^{-3}$, while the samples grown with C_2H_2 had a carbon concentration of about $5 \times 10^{18} \text{ cm}^{-3}$. To serve as a standard for comparison, we also examined a sample of bare (0001) sapphire crystal of the same grade as usually used as a substrate for GaN growth.

Luminescence measurements were carried out with the samples mounted in a liquid helium cryostat. The tunable light source for PLE spectroscopy was provided by a xenon lamp dispersed through a 0.25 m focal length double monochromator. The source for PL spectra was

either the xenon lamp/monochromator or the 325 nm line of a He-Cd laser, and the luminescence was analyzed by a 1 m focal length single grating monochromator and detected by a GaAs photomultiplier tube. The PL and PLE of a bare sapphire sample were measured under the same conditions as the GaN samples to determine whether the substrate could be responsible for some or all of the PLE signals measured from the GaN on sapphire samples.

RESULTS

A comparison of the low temperature PL spectra of the undoped GaN and C-doped GaN samples, excited above the bandgap at 3.81 eV, is shown in Fig. 1. The undoped GaN has weak YL, with peak intensity at 2.2 eV about 1000 times less than that of the exciton intensity at 3.47 eV. Also, the RL peak intensity, at 1.82 eV, is higher than that of the 2.2 eV YL in the undoped GaN. In contrast, the PL spectrum of the C-doped sample is dominated by YL, about 100 times weaker than the exciton intensity, while the RL of the C-doped GaN is just visible as a low energy tail on the YL peak.

As seen in Fig. 2 which shows PLE spectra detected at 2.2 eV, the bare sapphire, undoped GaN, and C-doped GaN all have similar, weak PLE in the 2.4 to 2.8 eV region. In the GaN sample, this suggests that the PLE in this range results from exciting light that passes through the GaN layer to excite 2.2 eV luminescence from the sapphire substrate. At exciting energies above 2.8 eV, the C-doped sample appears to have a PLE onset that cannot be attributed solely to the substrate, and possibly a second onset near 3.2 eV. The undoped GaN, which has much weaker YL than the C-doped GaN, does not exhibit a clear PLE onset above 2.8 eV, but rather exhibits a PLE spectrum remarkably similar to bare sapphire over the entire range of 2.3 to 3.3 eV. It is clear that extraction of the GaN PLE from the mixture of GaN and sapphire PLE is only possible for GaN with relatively strong YL and even then the GaN PLE can only be clearly distinguished in selected portions of the spectrum.

Fig. 3 shows PLE spectra of a bare sapphire substrate when detected at 2.43 eV, 2.19 eV, and 1.56 eV. When detected at the higher two energies, the sapphire exhibits a PLE

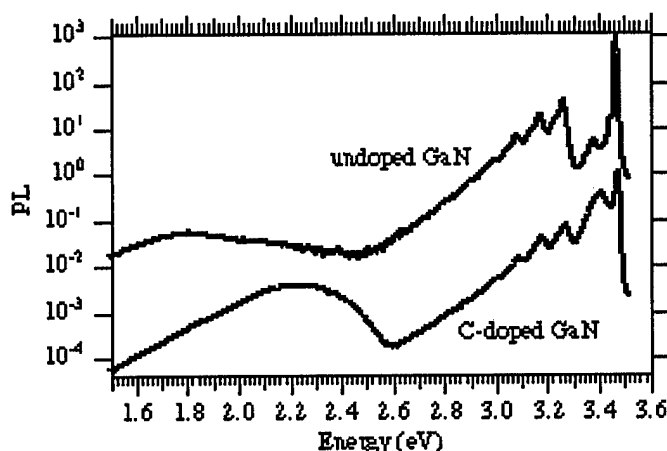


Figure 1. 5 K PL excited by He-Cd laser at 3.81 eV, comparing C-doped GaN and undoped GaN. Intensity has been scaled to 1 at the near-gap peak, and the curves have been offset vertically for viewing. The vertical axis is log-scaled.

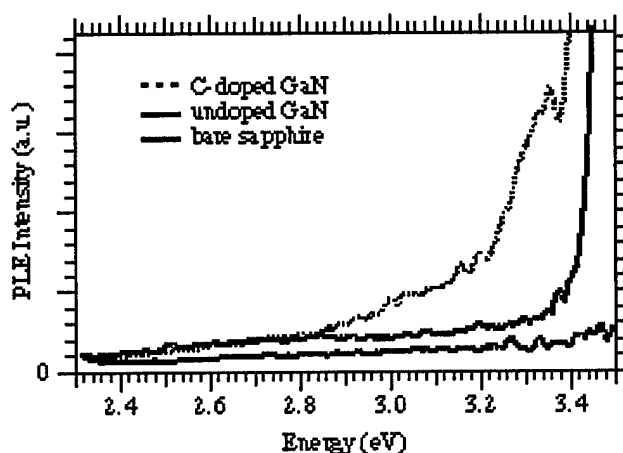


Figure 2. 5 K PLE spectra, detected at 2.2 eV, of C-doped GaN (top spectrum), undoped GaN (middle), and bare sapphire (bottom), each spectrum taken under identical conditions and corrected for the intensity spectrum of exciting light.

intensity which increases with increasing exciting light energy from 2.4 to 3.4 eV; however, when detecting at 1.56 eV the PLE intensity of the sapphire is significantly lower over the same spectral range. While the spectral shape and intensity of the sapphire PLE at the higher detecting energies in Fig. 3 is unfortunately quite similar to that which may be expected from GaN PLE spectra, the sapphire PLE detected at 1.56 eV is weaker which indicates that the substrate should contribute less to the GaN/substrate PLE mixture when detecting at 1.56 eV. These spectra and additional sapphire PL and PLE spectra have indicated that there is strong sapphire luminescence only in the range 1.6–1.8 eV and above 2.1 eV, so that PLE of RL from GaN on a sapphire substrate may be detected at or below 1.6 eV with little substrate contamination.

Fig. 4 compares PL spectra excited below the bandgap of GaN with 2.95 eV light for a sample of undoped GaN on a sapphire substrate and for a sample of bare sapphire. The sapphire has significant PL in the 2.1 to 2.5 eV range in addition to the characteristic sharp-line chromium emission between 1.65 and 1.8 eV. The YL from the GaN/sapphire sample has a PL spectrum which is almost identical to that of the sapphire. In particular, note that the PL intensity of the GaN/sapphire sample at 2.2 eV is less than double that of the bare sapphire sample, which clearly indicates that for GaN layers on sapphire, the PLE excited near 2.95 eV at best will be due to a mixture of luminescence from the substrate and the GaN layer, and at worst will be due almost entirely to the sapphire.

RL band PLE spectra of undoped GaN and C-doped GaN detected at 1.56 eV are shown in Fig. 5, as well as a PLE spectrum of bare sapphire for comparison. A broad RL excitation band extends from 2.1 to 2.8 eV for the C-doped sample and is virtually non-existent in the undoped GaN and the bare sapphire. A second C-doped sample which was grown with a different propane flow rate exhibits a nearly identical PLE band (not shown) to that of the C-doped GaN shown in Fig. 5. In contrast to the PLE of the YL, which was contaminated by substrate luminescence, the PLE of the RL from the C-doped GaN exhibits a clearly distinguishable excitation band which is nearly as strong as the band-edge PLE intensity. Any concerns that this PLE band could be substrate-

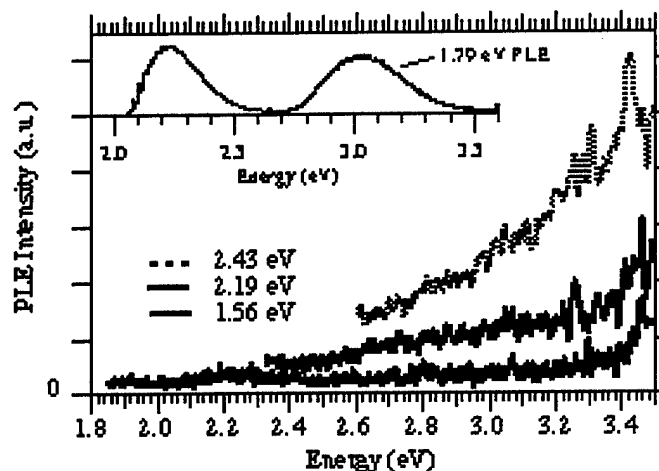


Figure 3. Comparison of the 5 K PLE of a bare piece of sapphire substrate when detecting at 2.43 eV, 2.19 eV, and 1.56 eV. The inset shows the sapphire PLE detected at 1.79 eV, which is a sharp Cr-related line. PLE spectra have been corrected for the intensity spectrum of the exciting light.

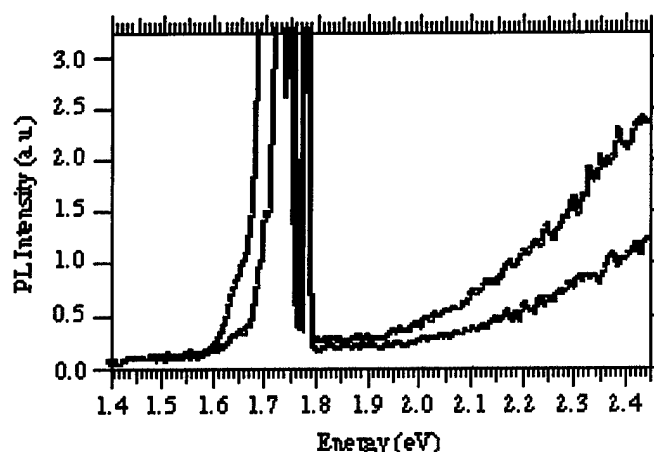


Figure 4. 5 K PL of bare sapphire and undoped GaN on a sapphire substrate, excited by 2.95 eV light. It is clear that the bare sapphire sample has luminescence in the 2.1 to 2.5 eV range. The chromium emission from the sapphire is visible in both spectra between 1.6 and 1.8 eV.

related are removed by noting that the chromium/sapphire PLE band which peaks at 3.0 eV is weak or non-existent in the PLE spectrum of the C-doped GaN. The unusual shape of the C-related excitation band suggests that it may result from two or more overlapping excitation bands. Two broad excitation peaks may be identified in the C-doped GaN PLE (Fig. 5), with peak energies near 2.3 eV and 2.6 eV, but the actual excitation mechanism could easily involve more than two overlapping processes which cannot all be distinguished in this PLE spectrum.

Since RL from the C-doped GaN was barely discernible on the tail of the YL in the above-gap-pumped PL spectrum (Fig. 1), we present for comparison a PL spectrum (Fig. 6) excited with 2.4 eV light, below the GaN band gap in the broad C-excitation-band. A RL band is clearly visible in the C-doped GaN when excited at this energy; however, the peak intensity occurs at 1.64 eV when pumped at 2.4 eV, as compared to a peak intensity at 1.82 eV in the undoped GaN when pumped above the gap. When PL is excited from the undoped GaN by 2.4 eV light another RL band appears, this one weak and broad with a peak at about 1.5 eV. RL luminescence would appear to be due to several different processes which result in emission in the 1.4 to 2.0 eV range, an assertion that is corroborated by the RL PLE spectrum (Fig. 5) which has an excitation band which appears to be a combination of two or more overlapping peaks.

Although no RL-related zero phonon line (ZPL) was observed from these GaN samples, it is worthwhile to estimate where the ZPL might occur if the RL emission and absorption bands are indeed strongly phonon-assisted, as may be expected for transitions involving energy levels deep within the bandgap. Comparing Fig. 5 and Fig. 6, we may estimate that the zero phonon line (ZPL) for RL emission and absorption could be near the midpoint between the onset of the emission and absorption bands which results in an estimate of 2.0 ± 0.2 eV for RL ZPL.

CONCLUSIONS

The interpretation of YL PLE spectra of GaN on sapphire substrates can be complicated by contamination of the GaN PLE with chromium-related luminescence from the sapphire substrate. As a result, YL PLE spectra of GaN on sapphire should be re-examined, preferably on samples which have had

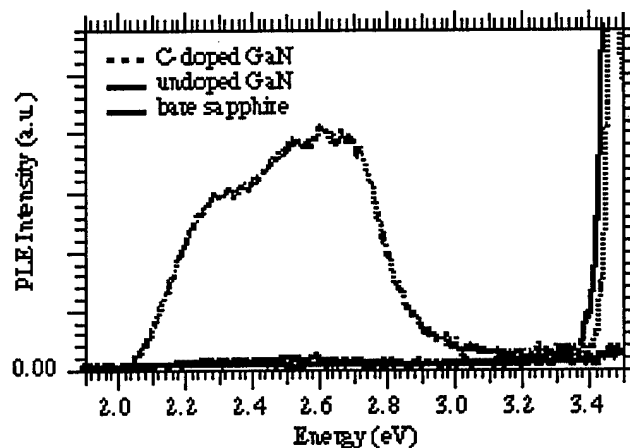


Figure 5. 5 K PLE of C-doped GaN, undoped GaN, and bare sapphire, detecting luminescence at 1.56 eV. Note the strong, multi-peaked excitation band of the C-doped GaN between 2.1 and 2.8 and the absence of this band in the undoped GaN and the bare sapphire. Spectra have been corrected for the intensity spectrum of the exciting light.

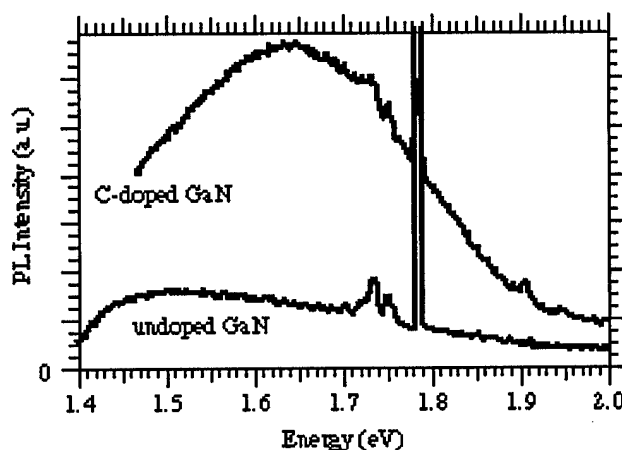


Figure 6. 5 K PL of C-doped GaN and undoped GaN, excited at 2.4 eV. The RL is now easily observed in the C-doped sample. There is also chromium emission from the sapphire substrate in the 1.7 eV to 1.8 eV range.

the substrate removed from the GaN epilayer. In contrast, the PLE of RL, which is observed in some HVPE grown GaN samples on sapphire substrates, is not significantly affected by the chromium substrate luminescence when detected at 1.6 eV and below and therefore may be studied with fewer complications than the PLE of YL in GaN on sapphire.

A strong, broad PLE band of C-doped GaN, detecting at 1.56 eV, has been observed for the first time. This RL band only appears clearly in the C-doped GaN when it is pumped in the broad band between 2.1 and 2.8 eV. If the RL is strongly phonon-assisted, it could have a ZPL with energy of 2.0 ± 0.2 eV. PL and PLE data suggested that RL may be excited by two or more overlapping PLE bands and RL emission may result from several overlapping luminescence bands including PL bands with peak energies near 1.5 eV, 1.64 eV, and 1.82 eV.

ACKNOWLEDGEMENT

This work was supported by NSF under the Engineering Research Centers Program (ECD 89-43166), DARPA (MDA 972-94-1-004), and the JSEP (0014-90-J-1270).

REFERENCES

1. J. I. Pankove and J. A. Hutchby, *J. Appl. Phys.* **47**, 5387 (1976).
2. T. Ogino and M. Aoki, *Jpn. J. Appl. Phys.* **19**, 2395 (1980).
3. D. M. Hofmann, D. Kovalev, G. Steude, B. K. Meyer, A. Hoffmann, L. Eckey, R. Heitz, T. Detchprom, H. Amano, and I. Akasaki, *Phys. Rev. B* **52**, 16702 (1995).
4. E. R. Glaser, T. A. Kennedy, K. Doverspike, L. B. Rowland, D. K. Gaskill, J. A. Freitas, Jr., M. Asif Khan, D. T. Olson, J. N. Kuznia, and D. K. Wickenden, *Phys. Rev. B* **51**, 13326 (1995).
5. R. Zhang and T. F. Kuech, *Appl. Phys. Lett.* **72**, 1611 (1998).
6. E. Calleja, F. J. Sanchez, D. Basak, M. A. Sanchez-Garcia, E. Munoz, I. Izpura, F. Calle, J. M. G. Tijero, and J. L. Sanchez-Rojas, *Phys. Rev. B* **55**, 4689 (1997).
7. J. Neugebauer, and C. G. Van de Walle, *Appl. Phys. Lett.* **69**, 503 (1996).
8. R. J. Molnar, K. B. Nichols, P. Maki, E. R. Brown, and I. Melngailis, *Mater. Res. Soc. Symp. Proc.*, **378**, 479 (1995).
9. W. Götz, L.T. Romano, B.S. Krusor, N.M. Johnson, and R.J. Molnar, *Appl. Phys. Lett.* **69**, 242 (1996).
10. S. J. Rhee, S. Kim, E. E. Reuter, S. G. Bishop, and R. J. Molnar, *Appl. Phys. Lett.* **73**, 2636 (1998).
11. R. Zhang and T. F. Kuech in *Nitride Semiconductors*, edited by F. A. Ponce, S. P. DenBaars, B. K. Meyer, S. Nakamura, and S. Strite (Mat. Res. Soc. Proc. **482**, Pittsburgh, PA, 1998) p. 709.
12. U. Kaufmann, M. Kunzer, C. Merz, I. Akasaki, and H. Amano in *Gallium Nitride and Related Materials*, edited by F. A. Ponce, R. D. Dupuis, S. Nakamura, and J. A. Edmond (Mat. Res. Soc. Proc. **395**, Pittsburgh, PA, 1996) p. 633.
13. S. Fischer, C. Wetzel, E. E. Haller, and B. K. Meyer, *Appl. Phys. Lett.* **67**, 1298 (1995).
14. M. Ilegems, R. Dingle, and R.A. Logan, *J. Appl. Phys.* **43**, 3797 (1972).
15. K. Maier, J. Schneider, I. Akasaki, and H. Amano, *Jpn. J. Appl. Phys.* **32**, 846 (1993).
16. U. Kaufmann, M. Kunzer, M. Maier, H. Obloh, A. Ramakrishnan, B. Santic, and P. Schlotter, *Appl. Phys. Lett.* **72**, 1326 (1998).
17. M. Banas, G. Liu, J. Ramer, K. Zheng, S. Hersee, K. Malloy in *Gallium Nitride and Related Materials*, edited by F. A. Ponce, R. D. Dupuis, S. Nakamura, and J. A. Edmond (Mat. Res. Soc. Proc. **395**, Pittsburgh, PA, 1996) p. 583.